



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C11D 3/20, 17/00, 3/37, 11/02, 17/06</b>	<b>A1</b>	(11) International Publication Number: <b>WO 95/20030</b> (43) International Publication Date: 27 July 1995 (27.07.95)
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(21) International Application Number: PCT/EP95/00226

(22) International Filing Date: 23 January 1995 (23.01.95)

## (30) Priority Data:

94200165.2 25 January 1994 (25.01.94) EP

(34) Countries for which the regional or international application was filed: AT et al.

94202818.4 29 September 1994 (29.09.94) EP

(34) Countries for which the regional or international application was filed: AT et al.

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(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: CO-GRANULES AND DETERGENT TABLETS FORMED THEREFROM

## (57) Abstract

A homogenous co-granule comprising a salt of a di-, tri- or tetracarboxylic acid and an inorganic acid salt. The salt of a di-, tri- or tetracarboxylic acid is preferably an alkali metal citrate or an alkali metal oxydisuccinate. The inorganic salt is preferably alkali metal silicate, in particular sodium disilicate or sodium silicate with a composition satisfying  $\text{SiO}_2 : \text{Na}_2\text{O} = 1.0 - 3.3$ , ideally  $1.8 - 2.3$ . The co-granule preferably also comprises at least one polymeric compound, being either acid and/or salt, selected from polycarboxylic acid and polypeptides. The invention also provides detergent compositions and tablets comprising these co-granules. The invention further provides the use of said detergent compositions and tablets in a mechanical dishwashing process.

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CO-GRANULES AND DETERGENT TABLETS FORMED THEREFROMFIELD OF THE INVENTION

This invention relates to co-granules useful in detergent compositions, and to the preparation of such co-granules.

- 5 The invention further relates to compacted forms of product produced from the granules, e.g. detergent tablets. More particularly, the invention relates to co-granules and tablets formed therefrom, especially of and for the use in automatic dishwashing compositions.

10 BACKGROUND OF THE INVENTION AND PRIOR ART

- As used herein, the term "co-granules" means granules comprising more than one compound or component of an overall cleaning system. The term "granule" is to be interpreted broadly and is intended to embrace various
- 15 particulate forms such as granulate, coarse powder, tablets and noodles. As used herein, the term "tablet" is to be construed as meaning a discretely shaped solid body of material, of which the shape and dimensions may vary with the application envisaged, and which may for
- 20 example have a weight in the range of from about 1 to about 100 grams, preferably from about 10 to about 50 grams.

- Dishwashing compositions are frequently made up from granules of one particular inorganic compound such as
- 25 e.g. alkali silicate and these compositions often contain other ingredients, especially organic compounds for example, in the form of different particles. The silicate granules for instance often dissolve only with difficulty and they lead to the formation of fines
- 30 (dust). The dissolution problem is aggravated by the fact that silicate granules having a  $\text{SiO}_2\text{:Na}_2\text{O}$  molar ratio between 1.8 and 3.0 and a moisture content of below about 18% dissolve only with considerable difficulty.

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Moreover, segregation of different kinds of granular components (e.g. a bleach system and enzymes) can occur.

Furthermore, alkali silicate granules with a homogeneous distribution of moisture are difficult to obtain, often as a consequence of the drying process, since less moisture tends to be present in the outer skin and more in the inside of the granules. This also reduces the solubility of the granules during use. Generally speaking, the preparation of granules of builder materials, e.g. phosphate-replacing builders like di-, tri- or tetracarboxylic acid and salts thereof, is difficult and therefore relatively expensive. The economics of granule manufacturing processes are therefore important.

Co-granules useful in detergent compositions are known inter alia from EP-A-0421664 (Rohm and Haas Company), which discloses a polymer-containing granulate containing at least 20% by weight of polymer and at least 20% by weight of a water-soluble inorganic compound. Such compounds are preferably sulphates, carbonates or silicates. In detergent compositions comprising the polymer-containing granules, other phosphate-replacing builders may also be present, such as zeolites, carbonates, nitrilotriacetic acid, citric acid, tartaric acid, salts thereof, phosphonates etc. The examples in the reference disclose granules containing polymer and sodium sulphate or sodium carbonate.

EP-A-0561452 (Unilever) discloses phosphate-free machine dishwashing compositions comprising a polyamino acid and an anti-scaling agent. Various builder salts may be included in the disclosed compositions, including preferably citrates, alkenylsuccinates, carbonates, bicarbonates, zeolites and mixtures thereof, but the

amount of a carbonate and/or bicarbonate builder in the composition is limited to 50% by weight.

5 CH-A-673033 (Cosmina AG) discloses phosphate- and trisodiumnitriloacetate-free alkaline machine dishwashing compositions comprising sodium citrate, at least one sodium salt of hydroxyethanediphosphonic acid and at least one sodium silicate.

10 JP-A-49076905 (Lion) discloses spray-dried powder detergents comprising, inter alia, inorganic and organic builder salts. In the agglomeration process, once granules of the desired uniform diameter are achieved, the agglomeration is stopped by treating them with a salt selected from a polyphosphate, carbonate, sulphate, silicate and/or sodium citrate.

15 JP-A-54106509 (Lion) discloses the preparation of spray-dried granulated detergent compositions comprising a surfactant, an alkali metal silicate salt and a phosphate salt. In the process the  $\text{SiO}_2:\text{M}_2\text{O}$  molar ratio in the silicate is controlled using an acid type surfactant or  
20 an organic acid such as citric acid.

It is one object of the present invention, therefore, to provide co-granules having good solubility in water, giving less fines during handling, having a more even distribution of moisture within the granules, preventing  
25 segregation of at least those ingredients included in the co-granules, and which can be prepared by convenient and economical techniques.

In the manufacture of granular and powder detergent products, various drying and/or granulation techniques  
30 are known.

In EP-A-0526978 for instance is disclosed the simultaneous drying and granulation of silicates in a turbine dryer, e.g. a turbogranulation dryer ex. Vomm-Turbo Technology, VOMM IMPIANTI E PROCESSI S.r.l., Milan, Italy. However, this dryer is less suited for the combined drying and granulation to produce co-granules containing substantial quantities of organic ingredients in conjunction with silicate. Due to the high attrition between the rotating blades and the film formed on the wall during the granulation phase, local overheating can cause partial decomposition of the organic ingredients, leading to (local-) colouring.

Drying can also conveniently be achieved by spray drying a slurry by a conventional technique using a spray tower in which the slurry is atomized and dried in a hot air stream. In order to obtain a granular detergent product, spray drying must be followed by a granulation step (e.g. using a Lödige Ploughshare mixer), optionally after milling. For granulation usually a small amount of moisture is added.

The powders obtained in a turbine dryer generally have a wider particle size distribution as part of the product gathers at the walls, creating larger particles. Furthermore powder particles obtained in a turbine dryer are less homogeneously dried as a result of the larger particles being more effectively dried at the outside than on the inside and as a result of the difference in residence time between particles remaining in the gas stream and those sticking on the (heated) wall of the dryer.

It is also possible to spray slurry onto fine particles while drying to form gradually growing granules. This can be performed in e.g. an AGT-unit for continuous

drying and granulation, ex Glatt-GmbH/Process Technology, Binzen, Lörrach, Germany.

Another possibility is to spray slurry in a rotary drum granulator onto fines to build up coarser particles, followed by, or in conjunction with, drying. Such spray-on techniques lead to granules with a more homogeneous distribution of moisture and consequently a better solubility.

It is a further object of the present invention, therefore, to provide a dried powder or granulated detergent product which shows less dust problem as a consequence of higher attrition resistance of the particles, a more homogeneous distribution of moisture in the particles, minimisation of the risk of segregation of various ingredients in the detergent compositions.

Dishwashing tablets are frequently produced from a mixture containing granules of one particular inorganic compound, such as e.g. alkali metal silicate, and additionally other ingredients, such as organic builder salts, as separate particles.

There are currently tablets on the market that contain citric acid or its sodium salt as an organic builder. It is known that such tablets may be easily fragmented or broken during handling due to the crystalline nature of the organic builder salt. This is especially evident for builder salt levels of more than 20% by weight and may become a serious problem for preferred builder salt levels of more than 30% by weight.

It has, therefore, been proposed to add binder material that can hold the tablet ingredients together so as to obtain stronger tablets. However, such binding material has a negative influence on the rate of tablet

~~dissolution such that cleaning performance during the~~  
washing cycle may be deteriorated.

It has been found that detergent tablets can more easily be formed if a fine grade or powder-form builder salt, such as sodium citrate, is used instead of the granular grades of sodium citrate that are normally used in machine dishwashing powders. However, increasing the level of fine citrate leads to poor flow properties of the base powder and, thus to poor die filling during the tableting process. As a consequence of this, a large variation in individual tablet weights is obtained.

It is yet a further object of the present invention, therefore, to provide detergent tablets which solve or ameliorate the above problems and particularly have adequate strength and dissolution properties.

#### SUMMARY OF THE INVENTION

Accordingly, in a first aspect the present invention provides a homogeneous co-granule comprising a salt of a di-, tri- or tetracarboxylic acid and an inorganic salt.

According to this first aspect, the invention also provides a process for the preparation of the above-defined co-granules, comprising preparing a slurry or solution of the ingredients of the co-granules, drying the mixture using any of various suitable known techniques, and granulating the resulting material.

In a second aspect the present invention provides a detergent composition comprising at least 25% by weight, preferably at least 40% by weight, more preferably at least 50% by weight, of co-granules according to the first aspect of the invention. Preferably the detergent



composition comprises a bleach system and/or an enzyme system. In preferred embodiments of this second aspect of the invention the detergent composition is formed from the co-granules, with or without other ingredients.

5 In a third aspect the present invention provides a detergent tablet comprising from about 25 to about 100% by weight, preferably from about 25 to about 90% by weight, of co-granules according to the first aspect of the invention. Preferably, the tablet includes a  
10 bleaching system and/or an enzyme system.

According to a fourth aspect, the present invention further provides the use of a co-granule containing granular detergent composition or detergent tablet according to the invention, in a machine dishwashing  
15 process.

#### DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The various aspects of the invention, and preferred features and embodiments thereof, will now be described  
20 in detail.

##### Co-granules

In the co-granules of the invention the salt of a di-, tri- or tetracarboxylic acid is especially an alkali metal salt of citric acid, mellitic acid, oxydisuccinic  
25 acid, carboxymethoxysuccinic acid, malonic acid, dipicolinic acid or alkenyl succinic acid. Part of the di-, tri- and tetracarboxylic acid component, e.g. up to about 30%, may if desired be replaced by a lower hydroxy monocarboxylic acid, e.g. lactic acid.

30 Partial salts of the di-, tri- or tetracarboxylic acid in which one or more of the hydrogen ions of the

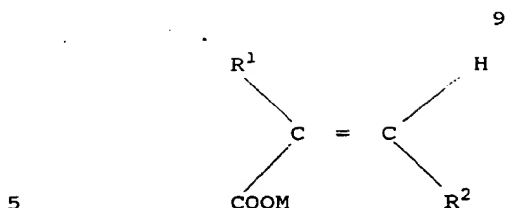
carboxylic groups are replaced by metal ions are particularly useful. Especially sodium and potassium salts can be used with good results for the purpose of the invention. Potassium salts are sometimes preferred because of their higher solubility. The use of alkali metal citrate, especially sodium citrate, in the co-granules according to the present invention is preferred. The use of sodium oxydisuccinate is also preferred.

The inorganic salt component of the co-granule of the invention is preferably selected from alkali metal silicate, alkali metal carbonate or bicarbonate, alkali metal sesquicarbonate, and mixtures thereof. Sodium silicate is a preferred inorganic salt and, when used, a composition satisfying  $\text{SiO}_2 : \text{Na}_2\text{O} = 1.0 - 3.3$ , preferably 1.8 to 2.8, e.g. 1.8 - 2.3, is particularly recommended. Alkali metal disilicates, in particular sodium disilicate, are especially preferred.

In other preferred embodiments of the co-granule of the invention the co-granule material also comprises at least one polymeric compound, being either acid and/or salt, selected from the group consisting of polycarboxylic acid polymers and polypeptides.

Suitable polycarboxylic acid polymers comprise e.g. a water-soluble homopolymer or copolymer having a molecular weight of at least 500. It may be derived from a monocarboxylic acid or from a di-, tri- or polycarboxylic acid. The polymer will normally be used in the form of its water-soluble alkali metal salt.

One group of polymer materials found to be of value comprises homopolymers derived from a monomer of the formula:



wherein  $\text{R}^1$  is hydrogen, hydroxyl,  $\text{C}_1\text{-C}_4$  alkyl or alkoxy, acetoxyl, or  $-\text{CH}_2\text{COOM}$ ;  $\text{R}^2$  is hydrogen,  $\text{C}_1\text{-C}_4$  alkyl or  $-\text{COOM}$  and M is an alkali metal. Examples of this group include the sodium and potassium salts of polyacrylic, polymethacrylic, polyitaconic, polymaleic and polyhydroxyacrylic acids and also the hydrolysis products of the corresponding polymerised acid anhydrides. Thus the polymer obtained by hydrolysis of maleic anhydride falls within this group.

15 A second group of suitable polymeric materials comprises the copolymers of two or more carboxylic monomers of the above formula. Examples of this group include the sodium and potassium salts of copolymers of maleic anhydride with acrylic acid, methacrylic acid, crotonic acids, itaconic acid and its anhydride and/or aconitic acid.

25 A third group of suitable polymeric materials comprises the copolymers of one carboxylic monomer of the above formula and two or more non-carboxylic acid monomers such as ethylene, propylene, styrene, alpha-methylstyrene, acrylonitrile, acrylamide, vinylacetate, methylvinylketone, acrolein and esters of carboxylic acid monomers such as ethyl acrylate and methacrylate.

Suitable polypeptides which can be incorporated in the co-granules according to the present invention include for example poly-aspartate and polyglutamate.

In further preferred embodiments of the co-granule of the

- invention the co-granule material also comprises at least one inorganic salt selected from the group consisting of alkali metal tripolyphosphate, alkali metal carbonate, alkali metal bicarbonate, alkali metal silicate, alkali metal sesquicarbonate and alkali metal sulphate. One of the advantages of incorporating such an inorganic salt is that it increases the solubility of the co-granule, especially if the co-granule contains silicates with  $\text{SiO}_2:\text{Na}_2\text{O} > 2.4$ , because these salts dissolve rapidly and thereby convert the co-granule into an open sponge-like structure so that the surface area of the co-granule is increased. This leads to an increase of the solubility of the remaining solid material of the co-granule. Most of the salts also act as a builder, reinforcing detergent activity. Non-phosphate inorganic salts such as various carbonates, especially alkali metal carbonate/bicarbonate/sesquicarbonate are preferred. In the co-granule the inorganic salts are usually present in the form of their lower stable hydrate(s).
- In particular preferred embodiments of the co-granule of the invention, the co-granule has the following composition (I) (all amounts being approximate):

I

- 1 (or 5) - 90% (w/w) alkali metal silicate, carbonate, bicarbonate or sesquicarbonate;
- 5 - 90% (w/w) alkali metal salt of di-, tri- or tetracarboxylic acid;
- 0 - 20% (w/w) polymer;
- 0 - 40% (w/w) alkali metal tripolyphosphate;
- 0 - 40% (w/w) alkali metal (bi)carbonate or sesquicarbonate;
- 0 - 20% (w/w) organic phosphonate;
- 0 - 60% (w/w) alkali metal sulphate;

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- 0 - 10% (w/w) of minor ingredients;
- 1 - 25% (w/w) moisture.

5 The organic phosphonates which can be present in the co-granule include for example those of the Dequest<sup>R</sup> range, which are especially added as builders to phosphate-free machine dishwashing compositions. A drawback of these polymers however is that some of them are not quite biodegradable and are therefore environmentally less acceptable. Therefore some of the polyphosphonates, 10 whilst being effective, are less acceptable as being P-containing products.

In especially preferred embodiments of the co-granule of the invention, the co-granule has the following composition (II) or alternatively the following 15 compositions (III) or (IV) (all amounts being approximate):

## II

- 20 - 50 (or up to 75)% (w/w) alkali metal silicate, carbonate, bicarbonate or sesquicarbonate;
- 20 25 (or 40) - 75% (w/w) alkali metal salt of di-, tri- or tetracarboxylic acid;
- 1 - 9% (w/w) polymer;
- 1 - 36% (w/w) alkali metal tripolyphosphate;
- 1 - 36% (w/w) alkali metal (bi)carbonate or 25 sesquicarbonate;
- 0 - 37 (or up to 60)% (w/w) alkali metal sulphate;
- 0 - 9 (w/w) organic phosphonate;
- 0 - 5% (w/w) of minor ingredients;
- 3 - 20% (w/w) moisture

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III

- 5-95% (w/w) alkali metal silicate, carbonate, bicarbonate or sesquicarbonate;  
0-60% (w/w) alkali metal salt of di-, tri- or  
5 tetracarboxylic acid;  
5-60% (w/w) polymer;  
5-25% (w/w) moisture.

IV

- 15-75% (w/w) alkali metal silicate, carbonate,  
10 bicarbonate or sesquicarbonate;  
25-85% (w/w) alkali metal salt of di-, tri- or  
tetracarboxylic acid;  
0-20% (w/w) organic phosphonate;  
0-60% (w/w) alkali metal sulphate;  
15 0-10% (w/w) nonionic surfactant;  
0-5% (w/w) of minor ingredients;  
1-25% (w/w) moisture.

- Under minor ingredients which may optionally be present in the co-granule of the invention are here to be  
20 understood various known adjunct materials commonly found in cleaning compositions, such as: enzyme stabilizers, such as the poly-alcohols, e.g. glycerol, and borax; anti-scaling agents; corrosion inhibitors, e.g. zinc salts, aluminium salts, benzotriazole, etc; crystal-  
25 growth inhibitors; threshold agents; thickening agents; anionic surfactants; perfumes and dyestuffs; preservatives.

- Also a small amount of preferably low- to non-foaming nonionic surfactant, which includes any  
30 alkoxyated nonionic surface-active agent wherein the alkoxy moiety is selected from the group consisting of

ethylene oxide, propylene oxide and mixtures thereof, is preferably used to improve the detergency and to suppress excessive foaming due to protein soil. However, an excessive proportion of nonionic surfactant should be avoided. Normally, an amount of up to 7% by weight, e.g. 0.1 to 5% by weight, preferably from 0.5 to 4% by weight, is quite sufficient.

Examples of suitable nonionic surfactants for use in the co-granule material of the invention are the low- and non-foaming ethoxylated straight-chain alcohols of the Plurafac<sup>R</sup> RA series, supplied by the Eurane Company; of the Lutensol<sup>R</sup> LF series, supplied by the BASF Company and of the Triton<sup>R</sup> DF series, supplied by the Rohm & Haas Company.

Although the particle size of the co-granules according to the present invention is not critical, co-granules are preferred which have an average particle size of from about 100 to about 1500 microns. More particularly there is a preference for co-granules having an average particle size of from about 300 to about 900 microns especially from about 500 to about 700 microns, and a Rosen Rammler N-value above about 2.5. Particle size determination and the definition and determination of the Rosen Rammler N-value are described in detail in "Small Particle Statistics" by Herdan, E; second revised edition; Butterworth, London 1960, in particular pp 86-101. Graph paper according to DIN 1171 (new) is often used to determine the N-value.

The present invention also provides, within its first aspect, a process for the preparation of the co-granules, which process comprises preparing a slurry of the ingredients of the co-granule and drying the mixture by means of suitable equipment, e.g. a turbine dryer such

as a turbogranulation drier ex-Vomm-Turbo Technology,  
Vomm Impianti E Processi S.r.l., Milan, Italy.

5 An alternative to drying using a turbine drier, and especially preferred, is spray-drying the slurry by a conventional technique using a spray tower in which the slurry is atomized and dried in a hot air stream. If desired, the resulting particles may be milled and/or restructured, for example in a granulation process, e.g. using a Lödige recycler, a Lödige plough share mixer, or 10 any other suitable apparatus, such as a twin roll compactor. Any restructuring stage does not need to be limited to the material produced by spray-drying and optionally then milled, which is used as an example only. The granulation process involves combining fine solid 15 particles like citrate, carbonates, sulphate, silicates, tripolyphosphate or co-granules as described above. Heat sensitive components of the granules, e.g. sodium bicarbonate, may also be added at this stage, as the temperature during granulation in e.g. a Lödige recycler 20 and a Lödige plough share mixer followed by fluid bed drying to remove excess moisture, should always be below about 100°C. This is much lower than with turbine driers which usually operate at around 300°C. Minor ingredients that are used in the final powder or granulate 25 formulation that are available in liquid or fine powder form, e.g. surfactant, perfume, dyes, organic phosphonate, corrosion inhibitors, may also be added as required. Turbine driers usually operate at around 300°C.

30 In a particularly preferred process the slurry is sprayed onto fine (recycled) particles and dried to form gradually growing co-granules. Particularly favoured are processes that separate fine particles from the coarser ones, preferably continuously, and recirculate the fines to the fluidized bed for further spraying-on. Particles



of the desired size can then be separated from the process at the appropriate time. Suitable equipment for continuous drying and granulation is e.g. an AGT-unit ex Glatt-GmbH/Process Technology, Binzen, Lorrach, Germany.

- 5 Another attractive possibility is to spray the slurry in a rotary drum granulator onto (recirculated) fines to build up coarser particles, followed by, or in conjunction with, drying. These spraying-on techniques lead to co-granules with a particularly homogeneous distribution of moisture, often better than for example those obtained by the use of a turbine dryer. Thus, such spraying-on techniques yield co-granules of a better solubility.

- 15 In the process of preparing the co-granules it is of course possible to use the various ingredients in the form of dry or hydrated solid forms and add water to form a slurry which is then processed as outlined above. It is however often advantageous to employ a process comprising preparing a slurry by adding di-, tri- or tetracarboxylic acid to a solution containing the inorganic salt(s), neutralizing the carboxylic acid(s) with alkali, optionally adding further ingredients, so as to obtain a slurry with a water content of from about 30 to about 60% (w/w), and converting the slurry into co-granules by any of the techniques described above, preferably by a granulation/drying technique.

- 30 Preferably, the co-granules of this aspect of the invention have a bulk density of at least about 700 g/dm<sup>3</sup>, more preferably above about 800 g/dm<sup>3</sup>, and most preferably a bulk density between about 900 g/dm<sup>3</sup> and about 1200 g/dm<sup>3</sup>. High bulk densities are desirable at present, to be able to provide final detergent compositions with a relatively high specific weight.

Detergent compositions

The present invention also provides, in a second aspect, a detergent composition which comprises at least about 25% by weight, preferably at least about 40% by weight, more preferably at least about 50% by weight of co-granules according to the first aspect of the invention. Preferably the composition includes a bleach system and/or an enzyme system, which usually may be added to the co-granules in the form of separate particles which may have the same particle size distribution as the co-granules. Also it is usually advantageous if the bulk density of the bleach/enzyme particles is comparable to that of the co-granules.

Preferred forms of detergent composition consist of at least about 50% by weight of the co-granules and less than about 30% by weight of a bleach system and an enzyme system. Preferably the detergent composition is non-irritant.

Enzymes are used for many purposes in various fields where biochemical reactions occur. In general, an enzyme can be described as a catalyst capable of permitting a biochemical reaction to quickly occur and can be classified according to the type of reaction they catalyze. Enzymes are characterized by high specificity; that is to say, each enzyme can catalyze a single reaction of one substance or a very small number of closely related substances.

Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil

or stain from the object being washed or to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removability. Well-known and preferred examples of these enzymes are proteases, lipases and amylases. Lipases are classified as EC class 3, hydrolases subclass EC 3.1, preferably carboxylic ester hydrolases EC 3.1.1. An example thereof are lipases EC 3.1.1.3 with the systematic name glycerol ester hydrolases. Amylases belong to the same general class as lipases, subclass EC 3.2, especially EC 3.2.1 glycoside hydrolases such as 3.2.1.1. alpha-amylase with the systematic name alpha-1,4-glucan-4-glucanohydrolase; and also 3.2.1.2, beta-amylase with the systematic name alpha-1,4-glucan maltohydrolase. Proteases belong to the same class as lipases and amylases, subclass EC 3.4, particularly EC 3.4.4 peptide peptido-hydrolases such as EC 3.4.4.16 with the systematic name subtilopeptidase A.

Obviously, the foregoing classes should not be construed as limiting the scope of enzyme-containing embodiments of compositions according to the invention. Enzymes serving different functions can also be used in the practice of this aspect of the invention, the selection depending upon the composition of biochemical soil, intended purpose of a particular composition, and the availability of an enzyme to degrade or alter the soil.

Lipases, sometimes called esterases, hydrolyze fatty soils. Lipases suitable for use herein include those of animal, plant and microbiological origin. Suitable lipases are also found in many strain of bacteria and fungi. For example, lipases suitable for use herein can be derived from *Pseudomonas*, *Aspergillus*, *Pneumococcus*, *Staphylococcus*, *Toxins*, *Mycobacterium Tuberculosis*, *Mycotorula Lipolytica*, and *Sclerotinia microorganisms*,

and can be made using recombinant DNA manufacturing techniques.

Suitable animal lipases are found in the body fluids and organs of many species. A preferred class of animal  
5 lipase herein is the pancreatic lipase.

Lipase may be employed in the present cleaning compositions in an amount of from about 0.005% to about 10%, preferably from about 0.01 to about 5% by weight of the composition, on a pure enzyme basis.

10 The enzyme most commonly used in machine dishwashing compositions are amylolytic enzymes.

The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in  
15 GB-A-1,296,839, cultivated from the strains of *Bacillus licheniformis* NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11 945, ATCC 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are amylolytic enzymes produced and distributed under the trade name of SO-95<sup>R</sup> or Termamyl<sup>R</sup>  
20 by Novo Industria A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram.

The amylolytic activity can be determined by the method  
25 as described by P. Bernfeld in "Method of Enzymology", Vol. I (1955), page 149.

The composition of this aspect of the invention preferably also contains a proteolytic enzyme.

Examples of suitable proteolytic enzymes are the

subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase<sup>R</sup>, supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase<sup>R</sup>, supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from Novo Industri A/S under the registered trade names of Esperase<sup>R</sup> and Savinase<sup>R</sup>. The preparation of these and analogous enzymes is described in GB-A-1243784.

Another suitable protease useful herein is a fairly recent commercial product sold by Novo Industri A/S under the trade name Durazym<sup>R</sup>, as described in WO-A-89/06279. The enzymes are generally presented as granules, e.g. marumes, prills, T-granules etc., and may have enzyme activities of from about 500 to 1700 glycine units/milligram. The proteolytic activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology", Vol. 22 (1938), page 79 (one Anson Unit/g = 733 Glycine Units/milligram).

All of these enzymes may each be present in a weight percentage amount of from about 0.2 to about 5% by weight, such that for amylolytic enzymes the final composition may have amylolytic activity of from about  $10^2$  to about  $10^6$  Maltose units/kg, and for proteolytic enzymes the final composition may have proteolytic enzyme activity of from about  $10^6$  to about  $10^9$  Glycine Units/kg.

Preferably enzyme material is present in the compositions of the invention in a total amount of up to about 10% by weight.

The detergent composition may also comprise a bleach system, which may or may not be encapsulated. The bleach system may be a chlorine- or bromine-releasing agent or a peroxygen compound. For environmental reasons, a peroxygen-based bleaching system is preferred. Suitable peroxygen compounds may be selected from alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonate, perphosphates, persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

Particularly preferred peroxygen compounds are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

Organic peroxy acids or the precursors therefor may also be utilized in the bleach system. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds. By "substantially water-insoluble" is meant herein a water-solubility of less than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-alpha-naphthoic acid;
- (ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxy lauric acid and

peroxystearic acid;

(iii) phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

- 5 (iv) 1,12-diperoxydodecanedioic acid (DPDA);  
(v) 1,9-diperoxyazelaic acid;  
(vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;  
(vii) 2-decyldiperoxybutane-1,4-dioic acid.

- 10 Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic  
15 peroxyacid precursor (SPCC) as described in US-A-4751015.

- Among suitable reactive chlorine- or bromine-oxidizing materials are heterocyclic N-bromo- and N-chloro imides such as tri-chloroisocyanuric, tribromoisocyanuric, dibromoisocyanuric and dichloroisocyanuric acids, and  
20 salts thereof with water-solubilizing cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethyl-hydantoin are also quite suitable.

- Dry, particulate, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium,  
25 sodium or calcium hypochlorite and hypobromite. Chlorinated trisodium phosphate is another suitable material. Chloroisocyanurates are, however, the preferred bleaching agents. Potassium dichlorosocyanurate is sold by Monsanto Company as ACL-59<sup>R</sup>. Sodium dichloroisocyanurates are also available  
30 from Monsanto as ACL-60<sup>R</sup>, and in the dihydrate form, from the Olin Corporation as Clearon CDB-56<sup>R</sup>, available in

powder form (particle diameter of less than 150 microns); medium particle size (about 50 to 400 microns); and coarse particle size (150-850 microns). Very large particles (850-1700 microns) are also found to be suitable also for encapsulation.

If desirable, a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US Patents 5,041,232 and 5,047,163, may be incorporated in the composition. Such bleach catalysts may suitably be presented in the form of a second encapsulate separately from the bleach capsule component.

For chlorine bleaches the amount of encapsulates used in the compositions of the invention may vary preferably within the range of from about 0.1 to about 10%, especially from about 0.5 to about 3% as available chlorine (Av Cl). For peroxygen bleaching agents a suitable preferred range will be from about 0.1 to about 20%, especially from about 0.1 to about 10%, preferably from about 0.5 to about 3 or 5% Av O (available oxygen).

In especially preferred detergent compositions according to the invention, in order that they are substantially non-irritant, the amount of peroxygen bleach, silicate and, carbonate, protease and surfactant taken together is at most about 20% by weight, more especially preferably between about 10 and 19.95% by weight of the composition.

#### Detergent Tablets

According to the third aspect of the present invention, there is provided a detergent tablet comprising from about 25 to about 100%, preferably from about 25 to about 90% by weight, more preferably from about 40 to about 90% by weight, of co-granules according to the first aspect



of the invention. The co-granules used to form the tablet are made by any of the processes described above.

The tablet of the invention preferably contains less than 35% by weight, preferably less than 20% by weight, of  
5 irritant material selected from peroxygen bleach, silicate, carbonate, protease and surfactant.

The strength of the tablet of the invention should preferably be high enough to allow handling without the need for individual wrapping.

10 The tablet strength is defined as the force, expressed in Newtons, needed to break the tablet, as measured using a Chatillon type UTM (remote 500) instrument in a direction perpendicular to the direction of compression.

The tablet strength should preferably be at least about  
15 150 Newton, more preferably at least about 200 Newton, so as to be sufficient for the tablet concerned to survive handling and packing. On the other hand, the tablet strength should not be too high, since in such a case the dissolution characteristics of the tablet concerned may  
20 not be adequate. The tablet strength should generally be below about 1000 Newton, preferably below about 800 Newton, more preferably below about 600 Newton, for round tablets. For rectangular tablets, the tablet strength should generally be below about 2000 Newton, preferably  
25 below about 1600 Newton, more preferably below about 1400 Newton.

The tablets of the invention preferably have a density of at least about 1300 kg/m<sup>3</sup>.

30 In order to achieve good cleaning performance, the tablets of this aspect of the invention preferably comprise more than about 20% by weight, preferably from

about 25 to about 50% by weight, of the salt of di-, tri-, or tetracarboxylic acid, as builder salt.

In a preferred embodiment the detergent tablet of this aspect of the present invention comprises (in  
5 approximate amounts):

- 25-90 %wt of the cogranule material;
- 5-20 %wt of a hydrogen peroxide source selected from alkali metal peroxides, organic peroxides, inorganic persalts, and mixtures thereof;
- 10 0-5 %wt of a bleach catalyst;
- 0-10 %wt of enzyme material;
- 0-5 %wt of tableting aids;
- 0-10 %wt of minor detergent ingredients.

It is usually advantageous if the bulk density and size  
15 distribution of the bleach and enzyme components of the tablet are comparable to that of the co-granule material.

The tablet of the invention may be effectively produced by a process involving the steps of mixing the co-granule material with the other ingredients of the tablet, and  
20 compacting the resulting detergent mixture using a pressure of at least 10 KN/cm<sup>2</sup>.

After having carried out the compaction step, difficulties may be encountered in releasing the just prepared tablet from the mould. These may be overcome by  
25 incorporating a minor amount (usually not more than 4% by weight) of any of the well-known mould release agents such as calcium stearate, talcum powder, siliconized talcum, stearic acid or paraffins. In this respect, it may also be helpful to incorporate nonionic surfactant  
30 into the tablet. Other suitable tablet-making aids which may be incorporated include glidants and lubricants such as sodium benzoate, fatty acids, fatty alcohols, starch

and polyethylene glycol.

### EXAMPLES

The invention will now be further illustrated by the following non-limiting examples. All parts and percentages mentioned are on a weight basis unless indicated otherwise.

#### Examples 1 and 2 (Preparation of co-granules)

Slurries were prepared having the following composition:

	<u>Composition (grams)</u>	
	<u>Example 1</u>	<u>Example 2</u>
Alkaline silicate solution (45%*)	302	1209
Sodium hydroxide solution (46%*)	190	763
Citric acid solution (48%*)	292	1170
Copolymer maleate/acrylate (Sokalan CP-5 ex BASF) solution (40%*)	56	225
Nonionic surfactant (Plurafac LF403)	8.5	-
Synthetic clay (Laponite powder)	8.5	34

(\* aqueous solutions)

The slurries of Examples 1 and 2 had a water content of 55% (w/w), with a low viscosity.

The slurries were dried using a laboratory scale spray tower, followed by restructuring (milling and spraying-on a few percent of a 45% alkaline silicate solution) and redrying.

The co-granules so obtained showed an excellent whiteness due to citrate which was translucent bound up in a white co-granule. Moreover the co-granules were easily soluble in water and showed an excellent dish washing performance.

Example 3 (Preparation of co-granules)

A slurry was prepared on a tonne scale having the following composition by adding the ingredients one after another:

5		<u>parts per weight</u>
	Citric acid solution (48%*)	90
	Sodium hydroxide solution (45%*)	58
	Copolymer maleate/acrylate solution (40%*)	12.5
	Alkaline silicate solution (45%*)	75.6

10 (\* aqueous solutions)

The moisture content of the slurry was 55% (w/w). It had a low viscosity. The slurry was dried using a pilot scale spray tower, yielding a powder with a moisture content of 12% (w/w), a bulk density of 400g/l and an average particle diameter of 400 $\mu$ m.

The powder was partly broken and restructured using a Lödige recycler and plough share mixer, yielding co-granules with a bulk density of 750 g/l and an average particle diameter of 550 $\mu$ m.

20 The appearance of the final product was pleasant. It dissolved and dispensed well in automatic dishwashing machines with a dissolution time of 1 minute at 20°C and a dispensing time of 4 minutes at 20°C. When compared with a product of the same composition obtained by dry mixing of components, these data were 3 minutes and 10 minutes, respectively.

Example 4 (Preparation of tablets from co-granules and comparative testing thereof)

5 The strength of detergent tablets produced from a detergent mixture not containing co-granules was compared with the strength of tablets according to the invention produced from a mixture having the same composition but containing co-granules.

First, co-granules were prepared having the following composition:

10	<u>Composition (parts by weight)</u>		
	<u>Example 4A</u>	<u>Example 4B</u>	
	Sodium citrate	40	30
	Maleate/acrylate copolymer <sup>(1)</sup>	6	6
	Sodium disilicate	26.2	5
15	Sodium bicarbonate	0	36.7

Note:

(1) this is Sokalan CP-5 ex BASF

These co-granules were prepared by a method comprising the following steps:

- 20 (1) preparing a slurry containing the constituents of the co-granules concerned, and having a moisture content of 55% by weight and a low viscosity;
- (2) drying the slurry using a pilot scale spray tower, yielding a powder with a moisture content of 12% by weight, a bulk density of 400 g/l and an average particle diameter of 400 microns;
- 25 (3) partly breaking and restructuring the powder using a mill, and a Lödige recycler and plough share mixer, yielding co-granules with a bulk density of 750 g/l and
- 30 an average particle diameter of 550 microns.

Subsequently, detergent tablets having a weight of 20 grams were made from mixtures containing the co-granules, by compacting these mixtures using a Fette Perfecta 3 tableting machine fitted with a 41 mm round die and optionally plastic inserts. The compaction pressure was 30 kN/cm<sup>2</sup>.

Using the same compacting method, 20 gram tablets (Comparative Examples 4C and 4D, respectively) were also made from mixtures not containing these co-granules but instead comprising the individual, non-co-granulated constituents thereof at concentrations equal to their respective concentrations in the co-granules-containing mixtures.

The compositions of the mixtures from which the tablets were produced were as follows (in % by weight):

<u>Example</u>					
<u>Example no</u>	<u>4A</u>	<u>4C</u> (Comparative)	<u>4B</u> (Comparative)	<u>4D</u> (Comparative)	
	Co-granules	72.2	-	77.7	-
20	Sodium citrate <sup>(2)</sup>	-	40	-	30
	Acrylate/maleate copolymer	-	6	-	6
	Sodium disilicate	-	26.2	-	5
	Sodium bicarbonate	-	-	-	36.7
25	perborate mono <sup>(3)</sup>	18	18	16	16
	Bleach catalyst granules <sup>(4)</sup>	2.8	2.8	2.4	2.4
	Enzymes <sup>(5)</sup>	5.4	5.4	3.3	3.3
30	Nonionic surfactant (Plurafac LF403)	1.5	1.5	1.5	1.5
	Perfume	0.1	0.1	0.1	0.1

Note:

- (2) for the comparative Examples, granular sodium citrate was used;
- (3) sodium perborate monohydrate;
- 5 (4) the composition of these granules was as follows:  
sodium carbonate 85% wt, acrylate/maleate copolymer (Sokalan) 5%wt, triazacyclononane based Mn-complex catalyst (as described in EP-A-458,397) 3% wt, moisture 7% wt;
- 10 (5) Savinase and Termamyl in a weight ratio of 5:3, ex NOVO.

The strength of the tablets produced was measured using a Chatillon type UTSM (remote 500) instrument. The measurement was carried out as defined hereinabove, i.e.

15 in a direction perpendicular to the direction of compression. The following tablet strength values, expressed in Newtons, were obtained:

<u>Example no</u>	<u>4A</u>	<u>4C</u> (Comparative)	<u>4B</u>	<u>4D</u> (Comparative)
20 Tablet strength	808	45	448	115

It can be concluded that the tablets according to the present invention have a considerably higher tablet strength than those of the comparative Examples.

The tablets of the invention took about 8 minutes to dissolve during a dishwashing cycle in a Bauknecht GSF 1161 automatic dishwashing machine.

\*\*\*\*\*



CLAIMS:

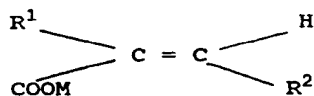
1. A homogenous co-granule comprising a salt of a di-, tri-, or tetracarboxylic acid and an inorganic salt.
- 5 2. A co-granule according to claim 1, wherein the salt of a di-, tri- or tetracarboxylic acid is an alkali metal salt of citric acid, mellitic acid, oxydisuccinic acid, carboxymethoxysuccinic acid, malonic acid, dipicolinic acid or alkenyl succinic acid.
- 10 3. A co-granule according to claim 1 or claim 2, wherein up to 30% of the di-, tri- or tetracarboxylic acid salt component is replaced by a lower hydroxy monocarboxylic acid.
- 15 4. A co-granule according to any one of claims 1 to 3, wherein the inorganic salt is selected from alkali metal silicate, alkali metal carbonate, alkali metal bicarbonate, alkali metal sesquicarbonate, alkali metal sulphate, alkali metal tripolyphosphate, and mixtures thereof.
- 20 5. A co-granule according to claim 4, wherein the inorganic salt is sodium silicate with a composition satisfying  $\text{SiO}_2 : \text{Na}_2\text{O} = 1.0 - 3.3$ .
6. A co-granule according to claim 5, wherein the sodium silicate has a composition satisfying  $\text{SiO}_2 : \text{Na}_2\text{O} = 1.8 - 2.8$ .
- 25 7. A co-granule according to claim 4, wherein the inorganic salt is sodium disilicate.
8. A co-granule according to any preceding claim, which further comprises at least one polymeric compound, being

either acid and/or salt, selected from the group consisting of polycarboxylic acid polymers and polypeptides.

9. A co-granule according to claim 8, wherein the polymeric compound is an alkali metal salt of a water-soluble homopolymer or copolymer having a molecular weight of at least 500 and derived from a mono-, di-, tri- or polycarboxylic acid.

10. A co-granule according to claim 9, wherein the polymeric compound is selected from the group consisting of:-

(i) homopolymers derived from a monomer of the formula:



wherein  $\text{R}^1$  is hydrogen, hydroxyl,  $\text{C}_1\text{-C}_4$  alkyl or alkoxy, acetoxy, or  $-\text{CH}_2\text{COOM}$ ;  $\text{R}^2$  is hydrogen,  $\text{C}_1\text{-C}_4$  alkyl or  $-\text{COOM}$ ; and M is an alkali metal;

(ii) copolymers of two or more carboxylic monomers of the above formula (i); and

(iii) copolymers of one carboxylic monomer of the above formula (i) and two or more non-carboxylic acid monomers selected from ethylene, propylene, styrene, alpha-methylstyrene, acrylonitrile, acrylamide, vinylacetate, methylvinylketone, acrolein and esters of carboxylic acid monomers.

11. A co-granule according to any preceding claim, which

further comprises up to 7% by weight of a low- to non-foaming nonionic surfactant.

12. A co-granule according to any preceeding claim , which has the following composition (I):

- 5 1 - 90% (w/w) alkali metal silicate, carbonate, bicarbonate or sesquicarbonate;
- 5 - 90% (w/w) alkali metal salt of di-, tri- or tetracarboxylic acid;
- 0 - 20% (w/w) polymer;
- 10 0 - 40% (w/w) alkali metal tripolyphosphate;
- 0 - 20% (w/w) organic phosphonate;
- 0 - 60% (w/w) alkali metal sulphate;
- 0 - 10% (w/w) of minor ingredients;
- 1 - 25% (w/w) moisture.

- 15 13. A co-granule according to claim 12, which has the following composition (II):

- 20 - 75% (w/w) alkali metal silicate, carbonate, bicarbonate or sesquicarbonate;
- 25 - 75% (w/w) alkali metal salt of di-, tri- or
- 20 tetracarboxylic acid;
- 1 - 9% (w/w) polymer;
- 1 - 36% (w/w) alkali metal tripolyphosphate;
- 0 - 60% (w/w) alkali metal sulphate;
- 0 - 9% (w/w) organic phosphonate;
- 25 0 - 5% (w/w) of minor ingredients;
- 3 - 20% (w/w) moisture.

14. A co-granule according to any preceding claim, which has an average particle size of from 100 to 1500 microns.

- 30 15. A co-granule according to claim 14, which has an average particle size of 500 to 700 microns and a Rosen

Rammler N-value above 2.5.

16. A co-granule according to any preceding claim, which has a bulk density of at least 700 g/dm<sup>3</sup>.

5 17. A process for preparing a co-granule according to any preceding claim, which process comprises preparing a slurry or solution of the ingredients of the co-granule, drying the mixture, and granulating the resulting material.

10 18. A process according to claim 17, wherein the drying step is carried out using a turbine drier or a spray drying apparatus.

15 19. A process for preparing a co-granule according to any of claims 1-16, wherein material prepared by the process of claim 17 or claim 18, or fine solid starting material comprising the ingredients of the co-granule is restructured.

20 20. A process according to any one of claims 17 to 19, which process comprises preparing a slurry or solution by neutralizing the di-, tri- or tetracarboxylic acid with alkali, adding the inorganic salt, optionally adding further ingredients, so as to obtain a slurry with a water content of 30 - 60% (w/w), and converting the slurry into co-granules.

21. A detergent composition comprising at least 25% of co-granules according to any one of claims 1 to 20.

25 22. A detergent composition according to claim 21, which further comprises a bleach system and/or an enzyme system.

23. A detergent composition according to claim 22,

comprising at least 50% of the co-granules and less than 30% of the bleach system and/or enzyme system.

24. A detergent composition according to claim 22 or 23, wherein the bleach system is a peroxygen bleaching system.

5 25. A detergent composition according to claim 24, wherein the amount of peroxygen bleach, silicate, carbonate, protease and surfactant taken together in the composition is at most 30%, preferably at most 20% by weight.

10 26. A method of making a detergent composition according to any of claims 21-25, wherein the composition is subjected to a tableting operation in a tableting apparatus.

27. A detergent tablet comprising from 25 to 100% by weight of co-granules according to any one of claims 1 to 16.

15 28. A detergent tablet according to claim 27, comprising from 40 to 90% by weight of the co-granule material.

29. A detergent tablet according to claim 27 or 28, which further comprises a bleaching system and/or an enzyme system.

20 30. A detergent tablet according to claim 29, which comprises less than 35%, preferably less than 20% by weight of irritant material selected from peroxygen bleach, silicate, carbonate, protease and surfactant.

25 31. A detergent tablet according to any one of claims 27 to 30, which has a strength of from 150 to 2000 Newton, as defined herein.

32. A detergent tablet according to any one of claims 27 to 31, which has a density of at least 1300 Kg/m<sup>3</sup>.

33. A detergent tablet according to any one of claims 27 to 32, which comprises more than 20% by weight of the salt  
5 of a di-, tri- or tetracarboxylic acid.

34. A detergent tablet according to any one of claims 27 to 33, which has the following composition:

25-90 %wt of the cogranule material;  
5-20 %wt of a hydrogen peroxide source selected from alkali  
10 metal peroxides, organic peroxides, inorganic persalts, and mixtures thereof;  
0-5 %wt of a bleach catalyst;  
0-10 %wt of enzyme material;  
0-5 %wt of tableting aids;  
15 0-10 %wt of minor ingredients.

35. A process for preparing a detergent tablet according to any one of claims 27 to 34, the process comprising the steps of mixing the cogranule material with the other ingredients of the tablet, and compressing the resulting  
20 mixture under a pressure of at least 10 kN/cm<sup>2</sup>.

36. Use of a co-granule according to any one of claims 1 to 16, or a detergent composition according to any one of claims 21 to 25, or a detergent tablet according to any one of claims 27 to 34, in a machine dishwashing process.

# INTERNATIONAL SEARCH REPORT

International Application No  
PC7, EP 95/00226

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/20 C11D17/00 C11D3/37 C11D11/02 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
------------	--	-----------------------

X	EP,A,0 561 452 (UNILEVER) 22 September 1993  see page 2, line 35 - line 49; claims; examples ---	1,2,4-9, 11, 21-24,36
X	EP,A,0 512 371 (DISPO KOMMERZ) 11 November 1992 see claims; examples 2-8 ---	1,2,5
X	CH,A,673 033 (COSMINA AG) 31 January 1990 cited in the application see page 3, column 1, line 48 - line 53; claims --- -/--	1,2,4,36

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

9 June 1995

Date of mailing of the international search report

21.05.95

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Grittern, A

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/JP 95/00226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9305, Derwent Publications Ltd., London, GB; Class D25, AN 93-043019 &amp; SE,A,9 100 760 (BARKSTROEM L H) 14 September 1992 see abstract</p> <p>---</p>	<p>1,2,4, 11, 21-24,36</p>
A	<p>DATABASE WPI Section Ch, Week 7513, Derwent Publications Ltd., London, GB; Class A97, AN 75-21529W &amp; JP,A,49 076 905 (LION FAT &amp; OIL CO LTD) 24 July 1974 cited in the application see abstract</p> <p>---</p>	<p>1,4,17, 18</p>
A	<p>PATENT ABSTRACTS OF JAPAN vol. 003, no. 128 (C-062) 24 October 1979 &amp; JP,A,54 106 509 (LION CORP) 21 August 1979 see abstract</p> <p>---</p>	<p>1,4,17, 18</p>
X	<p>EP,A,0 504 091 (VIKING IND.) 16 September 1992</p> <p>see claims; examples</p> <p>---</p>	<p>1,2, 4-10, 21-24, 27-29,36</p>
X	<p>US,A,3 951 877 (O. OKUMURA) 20 April 1976 see claims</p> <p>-----</p>	<p>1,2,17</p>



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 95/00226

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EP-A-0512371	11-11-92	DE-A-	4114956	05-11-92
CH-A-673033	31-01-90	NONE		
EP-A-0504091	16-09-92	NONE		
US-A-3951877	20-04-76	JP-C- JP-A- JP-B- DE-A-	873459 49029301 51047164 2336182	29-07-77 15-03-74 13-12-76 14-02-74

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